An Oxygen-Tolerant Visible Light Induced Free Radical Polymerization Using Mesoporous Graphitic Carbon Nitride

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Abstract

A novel oxygen-tolerant visible light photoinitiating system based on *in-situ* generation of Fenton reagents using mesoporous graphitic carbon nitride (*mpg*-C_3N_4) in conjunction with $FeCl_3 \cdot 6H_2O$, water and oxygen for free radical polymerization is described. A *mpg*-C_3N_4-catalysed photoinduced electron transfer reactions of water/oxygen and Fe^{3+} were demonstrated to enable generation of hydroxyl radicals that are capable of initiating the polymerization of mono and bifunctional monomers. The efficiency of the photoinitiation is controlled by specific surface area of the carbon nitride. Apparently, non-porous carbon nitrides did not yield polymers under the given conditions. Due to its heterogeneous nature, after the polymerization, although at lower rate, separated *mpg*-C_3N_4 could be used for further polymerizations.

Keywords: Photopolymerization, visible light, Fenton reagent, graphitic carbon nitride, oxygen inhibition

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Introduction

Photochemistry, particularly solar energy based photochemical reactions gained a vast interest as these reactions have high potential to meet the requirements of green chemistry.[1] In this context, photoredox catalysis using organic photoinitiators, dyes and nanoparticles has been employed in photoreactions as energy transducer. In particular, various nanoparticle based systems were shown to extend the photoactivation of both free radical and cationic polymerizations to the visible and even near infrared range.[2-10] Alternatively, a polymeric semiconductor, graphitic carbon nitrides (*g*-C_3N_4) emerged for similar purposes consisting mainly of carbon and nitrogen.[11, 12] These materials can be obtained from abundant nitrogen rich reagents such as melamine, urea, thiourea, cyanamide, dicyandiamide *etc.* and high surface areas can be attained by using a porogen as hard template *i.e.* silica nanoparticles during synthesis.[13-16]

Besides its synthetic simplicity, *g*-C_3N_4 is the most stable allotrope of carbon nitrides and also has rich surface properties. Therefore, *g*-C_3N_4 is a potent (photo)catalyst complementing carbon and metal oxides due to its unique electronic properties and relatively high surface area.[17, 18] This π-conjugated material exhibit suitable band gaps, depending on the synthesis conditions, which are suitable to perform photoredox reactions of oxygen and water, thus *g*-C_3N_4 is beneficial for water splitting, amine oxidative coupling reactions, dye and pollutant degradation, oxidation of alcohols and benzenes.[19-21] Moreover, on this semiconductor, photocatalytic production of H_2O_2 from water and oxygen under visible light is possible. [22, 23] Accordingly, alcohol/water mixtures and oxygen were efficiently converted to H_2O_2 on graphitic carbon nitride with very high selectivity (~90%). Electron spin resonance and Raman spectroscopy analysis revealed that the formation of hydrogen peroxide was through 1,4-endoperoxide species on the carbon nitride surface. Endoperoxide route suppresses one-electron reduction and thus reduces superoxide radical formation of O_2. On the other hand, this

pathway promotes two-electron reduction of O_2 to yield H_2O_2.[24, 25] Previously, such endoperoxide formation was also observed on anthracene derivatives upon irradiation in the presence of oxygen. Accordingly, by benefiting the photocatalytic activity of *g*-C_3N_4 to generate H_2O_2, photo-Fenton systems can be established with a suitable iron salt.[20] For example, Fenton-like heterogeneous photocatalysts were constructed via coupling Fe-containing polyoxometalate clusters with carbon nitride. [26-28] In another example, the decomposition of *p*-nitrophenol with H_2O_2 was performed by using Fe-doped C_3N_4/WO_3 hybrid structure as a photo-Fenton system.[29]

Fenton systems are mainly useful for environmental purposes to decompose organic pollutants,[30, 31] this unique chemistry has also found application in polymer syntheses field particularly in both free radical polymerizations or reversible addition–fragmentation chain transfer polymerizations (RAFT). By Fenton method, hydrogels, biomaterials, and core-shell particles for a wide range of applications were successfully fabricated.[32] On the other hand, the sole usage of mesoporous graphitic carbon nitride (*mpg*-C_3N_4) with tertiary amines as initiator in visible-light-induced free radical polymerization was demonstrated. The initiation mechanism relies on the photoinduced free radical generation by hydrogen abstraction on amine scarifying agents. [33-35] Similarly, the utilization of *g*-C_3N_4 as photoinitiator for hydrogel formations were also reported. Besides the photochemical activity, *g*-C_3N_4 entailed the role of a reinforcing agent for the obtained hydrogels.[36-38] Moreover, *g*-C_3N_4 was introduced into RAFT polymerization and linear polyacrylate, polymethacrylate as well as polyacrylamide have been obtained via photo-induced electron/energy transfer-reversible addition-fragmentation chain transfer (PET-RAFT) polymerization. The resulting polymers exhibited narrow molecular dispersities (*Đ*), and high end-group fidelity.[39, 40] Photoactivity of *g*-C_3N_4 in the absence of any radical abstracting species has been investigated which revealed the

formation of radical species on surface of *g*-C_3N_4 that can be utilized to alter surface properties.[41, 42]

However, in general, quenching of free radicals by molecular oxygen is one of the most challenging problems for both conventional and controlled/living polymerizations. Similarly, in the case of photopolymerizations, excited states of photoinitiators, especially Type II initiators, are strongly quenched by oxygen. Besides, oxygen scavenges both primary and propagating radicals resulting in the formation of less reactive stable peroxyl radicals. Therefore, several methods to prevent oxygen inhibition were proposed. For example, chemical strategies include use of specially designed reactive photoinitiators, [28, 43-47] enzymatic oxidation of glucose derivatives.[48-50]

In the present study, we take an alternative approach and focus on C_3N_4 and Fe^{3+} system as heterogeneous Fenton-like catalyst with high photoinitiation activity, long-term stability and low cost, which can be a promising method for performing photopolymerization under oxygen environment as a superior alternative to glucose oxidase/Fe^{2+} system.[51-53] Correspondingly, this paper reports the usage of *mpg*-C_3N_4/$FeCl_3 \cdot 6H_2O$ system as an heterogeneous photocatalyst to polymerize acrylates under oxygen.

Experimental

Materials: Acetone (HPLC grade, Sigma Aldrich), cyanamide (Sigma Aldrich), cyanuric acid (98%, Sigma Aldrich), ethanol (99.5%, Kanto Chemicals), melamine (99%, Sigma Aldrich), isopropyl alcohol (IPA) (99.7%, Sigma-Aldrich), Iron(III) chloride hexaaqua (98%, Acros Organics), sodium dodecyl sulfate (SDS) (99%, Thermo Fisher), anhydrous tetrahydrofuran (THF) (99,9%, Carlo-Erba), 1-decene (≥97%, Sigma-Aldrich), SiO_2 particles in water (Ludox HS-40, Sigma Aldrich), NH_4HF_2 in water (4 M, 95%, Wako Chemicals) were used as purchased. *N*-vinyl-2-pyrrolidone (NVP) (≥99%, Sigma-Aldrich) was distilled under vacuum prior to usage. (Methyl methacrylate (MMA) (98%, Sigma-Aldrich) and triethylene glycol

dimethacrylate (TEGDMA) (98%, Sigma-Aldrich), and 2-hydroxyethyl methacrylate (HEMA) (97%, Sigma Aldrich) were passed through a column containing basic alumina before use. Technical grade methanol was used for precipitating the formed polymers.

Characterization: All ^{1}H NMR spectra were recorded on an Agilent NMR System VNMRS 500 spectrometer at ambient temperature in $CDCl_3$ or DMSO-d_6 with $Si(CH_3)_4$ as an internal standard. FTIR spectra were recorded on a PerkinElmer FTIR Spectrum One spectrometer. Differential scanning calorimetry (DSC) was performed on PerkinElmer Diamond DSC from 30 to 320 °C with a heating rate of 10 °C min^{-1} under nitrogen flow. A typical DSC sample was 2−5 mg in a 30 μL aluminum pan. Gel permeation chromatography (GPC) measurements were performed on a Viscotek GPC max auto sampler system (Malvern, UK) consisting of a pump, a Viscotek UV detector, and Viscotek a differential refractive index (RI) detector with three ViscoGEL GPC columns (G2000H HR, G3000H HR, and G4000H HR, 7.8 mm internal diameter, 300 mm length) in series. Tetrahydrofuran (THF) was used as an eluent at flow rate of 1.0 mL·min^{-1} at 30 °C. Both of the detectors were calibrated with poly(methyl methacrylate) (PMMA) standards having narrow-molecular-weight distribution. Data were analyzed using ViscotekOmniSEC Omni-01 software (Malvern, UK). X-ray diffraction (XRD) patterns were obtained using Bruker D8 Advance X-ray diffractometer via Cu-Kα radiation. Scanning electron microscopy (SEM) was performed using JSM-7500F (JEOL). Solid state ultraviolet-visible (UV-Vis) spectroscopy was recorded via a Cary 500 Scan spectrophotometer equipped with an integrating sphere.

Preparation of *g*-C_3N_4: g-C_3N_4 was synthesized as reported in literature.[54] 1.0 g of cyanuric acid and 1.0 g of melamine were mixed with 40 mL distilled water and shook overnight for supramolecular complex formation. After centrifugation at 5000 rpm for 5 minutes, a

precipitate was dried at 60 °C under vacuum overnight. The dried product was transferred into a capped crucible and put into N_2 protected oven at 550 °C for 4 hours, with a heating rate of 2.3 °C·min^{-1}. (Surface area (BET) ≈ 65 m^2/g)

Preparation of 1-decene functional *g*-C_3N_4: Photo-grafting 1-decene to *g*-CN was achieved as reported previously.[55] 200 mg *g*-CN was weighted in a glass vial with magnetic stirrer, 2 g 1-decene and 2 g IPA were added. The mixture was sonicated for 10 minutes and nitrogen was flushed through the mixture for 3 minutes for the removal of dissolved oxygen. The mixture was placed between two 50W LED daylight sources (20 cm apart from each other) and stirred continuously for 3 hours at 50 °C. Afterwards, the mixture was vacuum filtered, washed 3 times with IPA (2×40 mL) and washed once with acetone (10 mL). After filtration, the solid sample was dried under vacuum at 50 °C overnight. (Surface area (BET) ≈ 18 m^2/g) (See supplementary material Figure S1 for SEM pictures)

Synthesis *mpg*-C_3N_4: According to the literature,[56] a unity mass ratio of silica to cyanamide was used to synthesize *mpg*-C_3N_4. Cyanamide (20 g) was dissolved in a 40 wt% dispersion of 12 nm SiO_2 particles in water (50 g) with stirring at 80 °C for about 3 h to evaporate the water. The resulting white powder was then heated at a rate of 2.3 K min^{-1} over 4 h to reach a temperature of 550 °C, and then held at this temperature for an additional 4 h. The resulting brown-yellow powder was stirred in 200 mL of 4 M NH_4HF_2 for 2 h, followed by filtration and washing with 100 mL of H_2O and 50 mL of ethanol. This washing cycle was repeated to completely remove the silica template. The powder was then stirred in 200 mL of H_2O for 2 h, then filtered and washed with H_2O and ethanol. Finally, the powders were dried at 120 °C overnight. The yield of *mpg*-C_3N_4 was ~40%, based on carbon content. (Surface area (BET) ≈ 210 m^2/g) (See supplementary material Figure S2 for SEM pictures)

Typical Photopolymerization Procedure: For a typical photopolymerization reaction 2.7 mg of $FeCl_3 \cdot 6H_2O$ (2 mmol) was dissolved in 0.5 mL:0.5mL anhydrous THF:water mixture in a 25 mL Schlenk tube. Then 5 mg of *g*-C_3N_4 was added to this solution together with 1000 μL MMA (9.25 mmol) and 2.8 mg of sodium dodecylsulfate. The reaction mixture was irradiated in a Rayonet photochemical reactor equipped with 6 fluorescent light bulbs emitting light between 400 and 500 nm (λ_{max}= 450nm) for 4 hrs. The reaction mixture was added dropwise in 15-fold excess (30 mL) of methanol and the precipitated polymer was filtered, washed with cold methanol and then dried in a vacuum chamber for 24 h at ambient temperature.

Photo-DSC Procedure: 3 mg (~10 mmol) of TEGDMA together with 2 mg of *g*-C_3N_4 and 0.5 mg of $FeCl_3 \cdot 6H_2O$ was placed inside a Photo-DSC pan. Then, the pan was irradiated between 320–500 nm at constant temperature (30 °C) until the polymerization was completed (5 min.). The conversion (C) was calculated by using the formula $C=\Delta H_t/\Delta H_0$, where ΔH_t is the reaction heat evolved at time t and ΔH_0 is the theoretical heat for complete conversion. ΔH_0 for TEGDMA is 81.40 kJ mol^{-1}.[57-61]

Results and Discussions

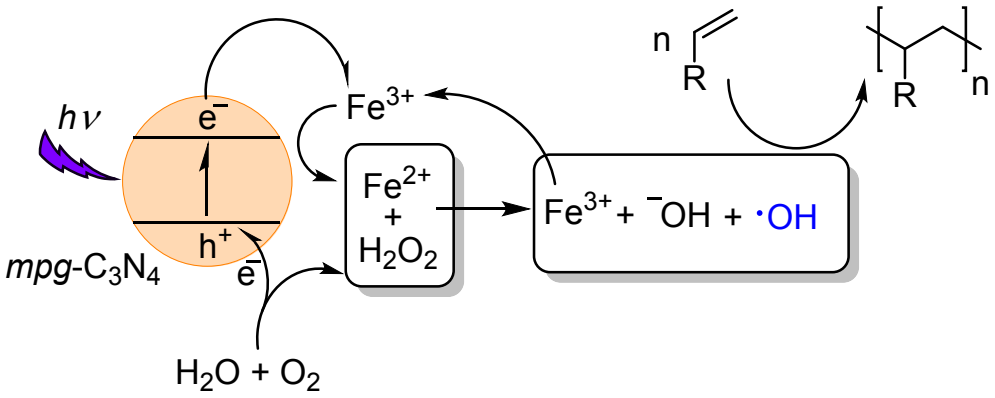
Since the first description of the Fenton reaction by H. J. H. Fenton in 1894,[30] this reaction found several applications ranging from wastewater treatment to polymer chemistry or even biosensors and cancer therapeutics.[32] The Fenton reaction generates hydroxyl radicals (HO•) by a spontaneous redox via electron transfer from Fe^{2+} species to H_2O_2 (Scheme 1).[62] These hydroxyl radicals are expected to have the similar behavior as the hydroxyl radicals produced

by peroxides and therefore have been used as radical initiator in vinylic polymerization or grafting for several decades.[63, 64]

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{-}OH + {}^{\cdot}OH$$

Scheme 1. Simplified presentation of the Fenton reaction

Alternatively, the Fenton system can be established by generating H_2O_2 via reducing O_2 and oxidizing water through *g*-C_3N_4 under visible light.[65] Concomitantly, Fe^{3+} can be reduced to Fe^{2+} by photo ejected electrons of *g*-C_3N_4. Thus, all the required components of the Fenton reaction can be produced *in-situ* by visible light and the formed hydroxyl radicals can eventually act as free radical initiator to polymerize vinyl monomers (Scheme 2). By the described method, oxygen inhibition can be succeeded via its consumption on the surface of *mpg*-C_3N_4 as endoperoxide to generate H_2O_2.



Scheme 2. Photopolymerization of vinyl momoners under visible light (400–500 nm) through *mpg*-C_3N_4 generated Fenton system.

Accordingly, in this study, methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA) and *N*-vinyl-2-pyrrolidone (NVP) were polymerized in open vessels without prior deoxygenation under visible light between 400–500 nm. The irradiation wavelength was selected according to the absorption of *mpg*-C_3N_4 (Figure 1a). The efficiency of the photo-

initiating system in the photo-curing of a di-functional monomer (TEGDMA) was also studied. The heat released during the curing of the formulations was traced by a photo-curing system incorporated to differential scanning calorimetry (Photo-DSC). Polymerization exotherms of TEGDMA under irradiation between λ = 320–500 nm is shown in Figure S3. The shape of the polymerization exotherms indicate the existence of two major stages as a rapid first stage followed by a slow stage. At the second stage, gelation and vitrification of the polymerizing di-functional monomer most likely retard the diffusion of the components to the propagating chains thus an apparent deceleration occurs. A similar experiment was performed in a test tube and the gelation of TEGDMA after photopolymerization can be seen in Figure 1b.

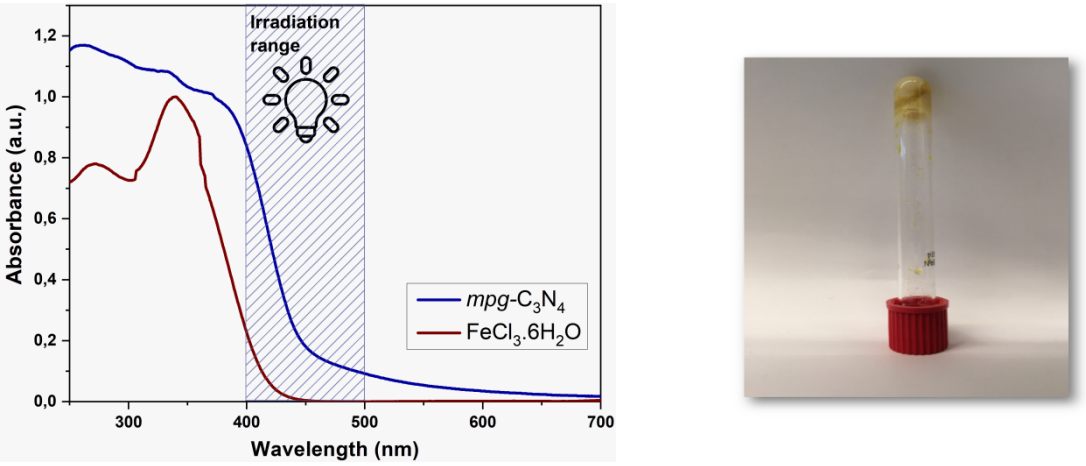


Figure 1. UV-vis absorbance of *mpg*-C_3N_4 and $FeCl_3 \cdot 6H_2O$ (band showing the irradiation wavelength) (a), photo showing the gelation of TEGDMA after photopolymerization in the presence of *mpg*-C_3N_4 and $FeCl_3 \cdot 6H_2O$ (b).

In comparative studies, similar experiments were performed without oxygen, water, $FeCl_3 \cdot 6H_2O$ and *mpg*-C_3N_4 by excluding one of these ingredients in each experiment and it was observed that each of these components have a crucial role in the initiation process as polymerization did not succeed in the absence of these materials. Here, water played a dual role both as solvent for $FeCl_3 \cdot 6H_2O$ and as reagent to produce H_2O_2 by acting as electron donor for the electron hole (h^+) on *mpg*-C_3N_4. However, unlike other monomers MMA could only be

polymerized by adding emulsifier (SDS) into the reaction medium to prevent phase separation between MMA and THF-water solvent mixture. Moreover, *mpg*-C_3N_4, *g*-C_3N_4 and *g*-C_3N_4-decene were used in the experiments to reveal the effects of surface area and surface properties on the photopolymerization. According to the experimental results, surface area has a high impact both on polymerization times and monomer conversions. Although *g*-C_3N_4 system was active to initiate polymerization, the conversions for each monomer were relatively low compared to *mpg*-C_3N_4 system (Figure 2). This finding can possibly be explained by the porous nature of *mpg*-C_3N_4, because in similar attempts with non-porous *g*-C_3N_4-decene polymerization were unsuccessful, although *g*-C_3N_4-decene has an improved dispersibility in the reaction medium due to decene functionalities on the surface of C_3N_4. Thus, the porosity plays a critical role in this designed system by increasing the adsorption area for $FeCl_3 \cdot 6H_2O$ to provide enough chance to interact with the surface of C_3N_4 for reduction of Fe^{3+} and accordingly most of the initiation takes place in the pores that can be considered as confined volumes. On the other hand, decene groups may reduce the endoperoxide formation on the surface and inhibit the H_2O_2 formation or could attenuate the electron transfer between the surface of carbon nitride and $FeCl_3$ particles and these possibilities could be the other causes of inefficacy of *g*-C_3N_4-decene system in Fenton based photopolymerization. The exact mechanism is not known thus all these possible events may act individually or collectively.

In a relatively short polymerization period (210 seconds) approximately 39% conversion was obtained with *mpg*-C_3N_4 for TEGDMA. However, the conversions for MMA, NVP, HEMA were between 16–20 % for polymerization a time of 240 min. (Table 1). Here it can be discussed that the conversions could be considered as relatively low compared to classical Fenton based polymerization even in the case of the *mpg*-C_3N_4 system. On the other hand, such conversions could be expected since the system is heterogeneous and in the course of polymerization the

monomer diffusion into the pores could slow down due the increasing viscosity of the medium in the pores.

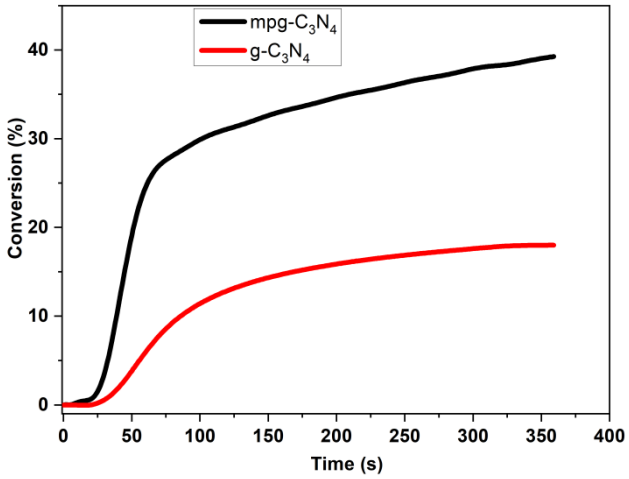


Figure 2. The conversions of TEGDMA with *mpg*-C_3N_4 and *g*-C_3N_4 Fenton systems.

Apart from oxygen inhibition, an additional advantage of the described initiating system is the simple separation of *mpg*-C_3N_4 from the mixture by filtering the solid after the polymerization. The *mpg*-C_3N_4 was purified by washing THF and water and reused as photoinitiator in further polymerizations. The residual iron salts could be removed completely from the pores of catalyst due to the excellent solubility of $FeCl_3$ in water. The comparative XRD spectra of $FeCl_3 \cdot 6H_2O$ and washed *mpg*-C_3N_4 is depicted in Figure 3a and the signals of $FeCl_3$ is undetectable in the XRD spectrum of *mpg*-C_3N_4 showing the efficiency of simple washing procedure to purge the pores. Although *mpg*-C_3N_4 and *g*-C_3N_4 are effective heterogeneous photo-catalysts and removal of $FeCl_3$ is relatively easy for the described photo-Fenton system, recycled carbon nitrides were not as efficient as the first use (Table 1). The monomer conversions dropped down to between 5 and 8% probably due to the deterioration of the carbon nitride surface through endoperoxide formation mechanism. Because these endoperoxides could react with double bonds of the monomers and the surface of carbon nitride could chemically bind to these organics. A minor part of the monomer could also attach to the surface directly in grafting from fashion.[66] Only

small amount of such surface deterioration would reduce the planarity of the surface causing a decrease in photoactivity for this specific system. Furthermore, irreversible bonding of monomers to the surface could potentially deactivate catalytic centers.

Table 1. Visible Light-induced photopolymerization[a] results of different monomers using *mpg*-C_3N_4 in the presence of aqueous THF solution of $FeCl_3 \cdot 6H_2O$.

Photocatalyst	BET (m^2/g)	Monomer	Wavelength (nm)	Time (min)	Conversion (%)	M_n[g] (kg/mol)	$Đ$[g]
g-C_3N_4	65.12	TEGDMA	400–500	240	~ 35[d]	∞	-
g-C_3N_4	65.12	TEGDMA	320–500[c]	5	18[f]	∞	-
g-C_3N_4	65.12	MMA[b]	400–500	240	11[d]	31.1	1.28
g-C_3N_4	65.12	MMA[b] after recycle	400–500	240	5[d,e]	31.8	1.37
g-C_3N_4	65.12	HEMA	400–500	240	12[d]	1.2	1.34
g-C_3N_4	65.12	NVP	400–500	240	18[d]	3.0	1.05
mpg-C_3N_4	211.45	TEGDMA	400–500	240	~ 39[d]	∞	-
mpg-C_3N_4	211.45	TEGDMA	320–500[c]	5	39[f]	∞	-
mpg-C_3N_4	211.45	MMA[b]	400–500	240	18[d]	12.1	1.56
mpg-C_3N_4	211.45	MMA[b] after recycle	400–500	240	8[d,e]	22.3	1.62
mpg-C_3N_4	211.45	HEMA	400–500	240	16[d]	2.1	1.71
mpg-C_3N_4	211.45	NVP	400–500	240	20[d]	2.8	1.07

[a] Conditions: *g*-C_3N_4 = 5 mg, $FeCl_3 \cdot 6H_2O$ = 2.7 mg (0.01mmol), monomer = 10 mmol, solvent = 0.5 mL:0.5 mL THF:water mixture., T= 25 °C except Photo-DSC studies realized at 30 °C. [b] Polymerization in the presence of 2.8 mg emulsifier; SDS. [c] The mixture was irradiated for 5 min. in Photo-DSC experiments. [d] Determined gravimetrically. [e] Determined gravimetrically after the polymerization with recovered *mpg*-C_3N_4. [f] Conversion was calculated from photo-DSC. [g] Determined by gel-permeation chromatography (GPC) calibrated with PMMA standard.

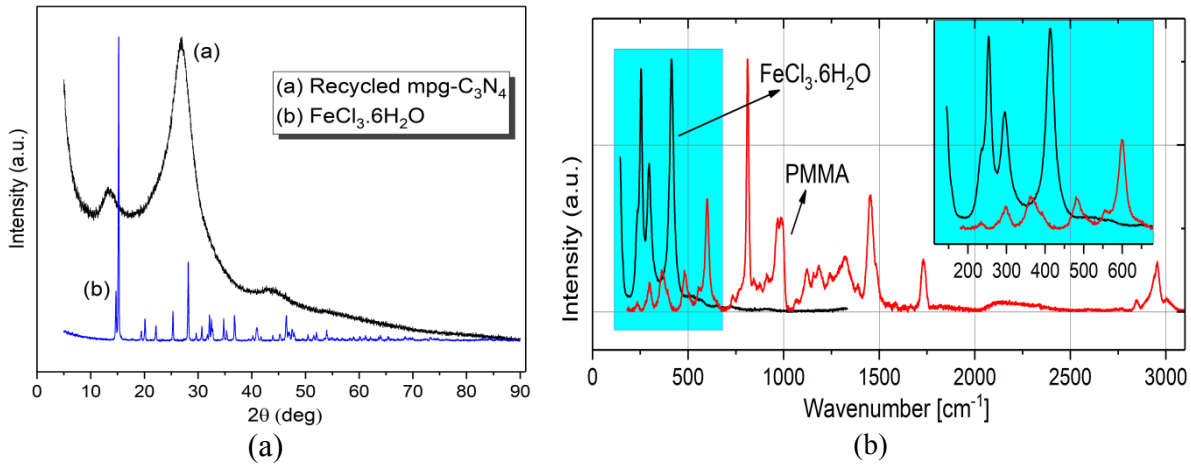


Figure 3. XRD spectra of recycled *mpg*-C_3N_4 and $FeCl_3 \cdot 6H_2O$ (a), Comparison of the Raman spectra of synthesized PMMA and $FeCl_3 \cdot 6H_2O$ (b).

Apart from recycling issue, possible iron salt contamination was analyzed for the obtained polymers after precipitating the polymers in methanol and subsequent washing with methanol and water. As it is well known, ferric chlorides exhibit sharp and distinctive signals in Raman spectroscopy and thus the residual iron chlorides can be traced by comparing the Raman spectra of obtained polymer and $FeCl_3 \cdot 6H_2O$.[67] In Figure 3b, the overlaid Raman spectra of synthesized poly(methyl methacrylate) (PMMA) and $FeCl_3 \cdot 6H_2O$ is depicted and the results clearly show that iron salt contamination in PMMA is below detection limit of Raman spectroscopy.

In conclusion, photoinitiation of free radical polymerization under oxygen atmosphere could be efficiently achieved between 400–500 nm by using *mpg*-C_3N_4/Fe^{3+} system. In the process, a photo Fenton system was established by generating H_2O_2 through simultaneous reduction of O_2 and oxidation of water. Moreover, Fe^{3+} was reduced to Fe^{2+} by electron transfer from the conduction band of *mpg*-C_3N_4. The generation of initiating hydroxyl radicals occurs by the Fenton reaction of the *in-situ* formed components. The effect of each factor, oxygen, surface area, $FeCl_3 \cdot 6H_2O$, water was evaluated and found to be supporting the proposed mechanism. Moreover, it should be noted that the initiating system overcomes the odor, toxicity and

migration problems generally encountered with low molar mass photoinitiators. Also, effective removal of iron salts from both *mpg*-C_3N_4 and the resulting polymers limits the iron contamination possibilities in the final-structures. Besides, the excellent light absorption properties in the visible range facilitated by the large surface area of *mpg*-C_3N_4 make these types of photoinitiators valuable for many targeted applications.

Supplementary Material

Supplementary Material is available ……..

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

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Supplementary material for

An Oxygen-Tolerant Visible Light Induced Free Radical Polymerization Using Mesoporous Graphitic Carbon Nitride

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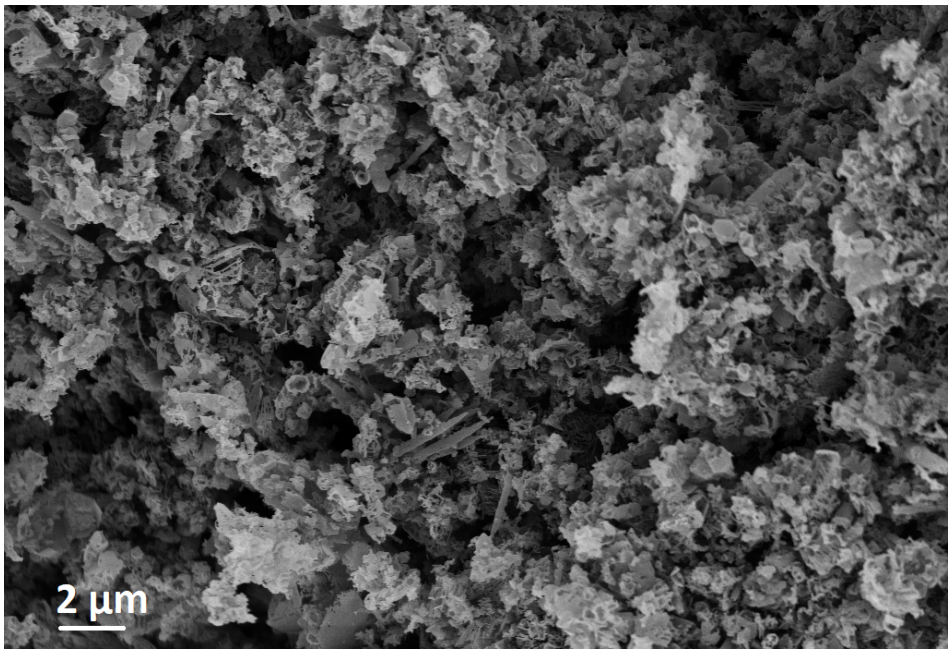


Figure S1: SEM image of *g*-C_3N_4-decene.

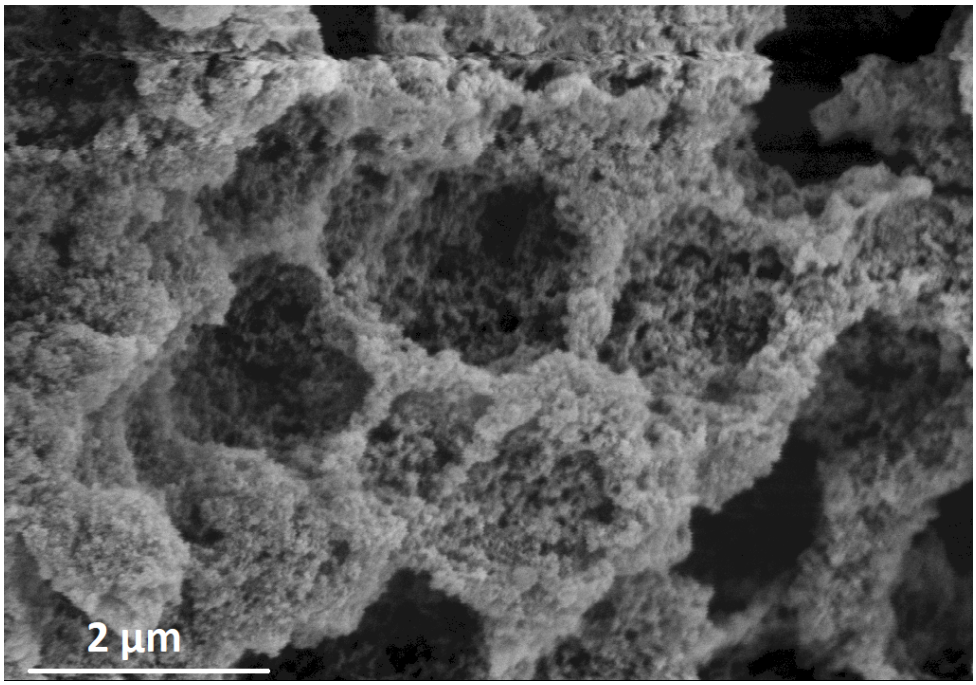


Figure S2: SEM image of *mpg*-C_3N_4.

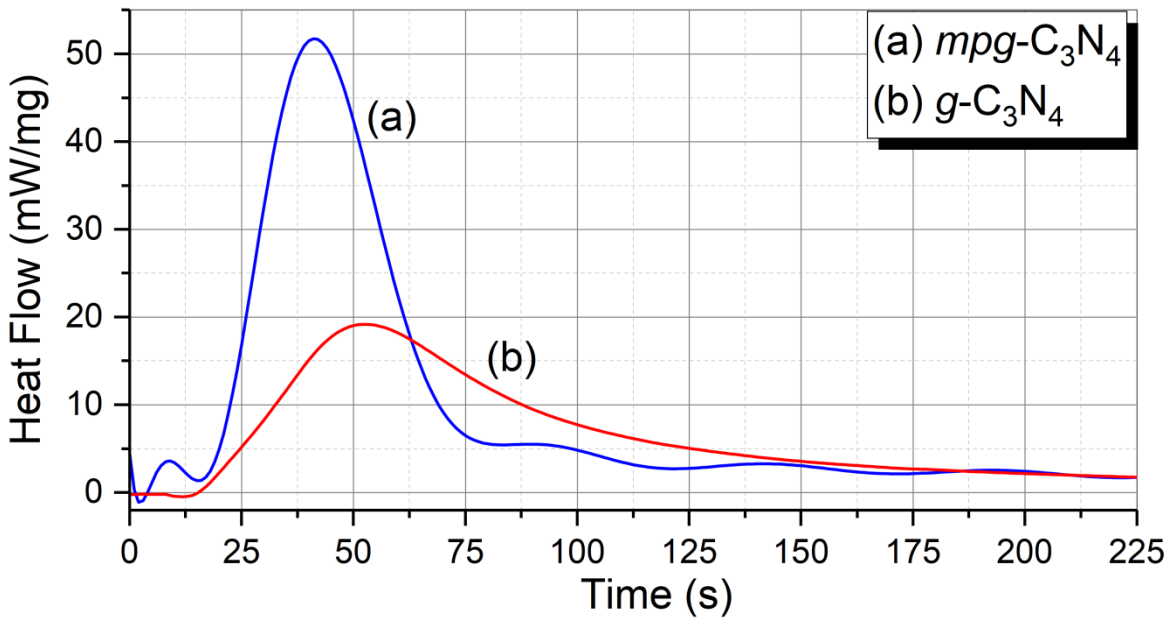
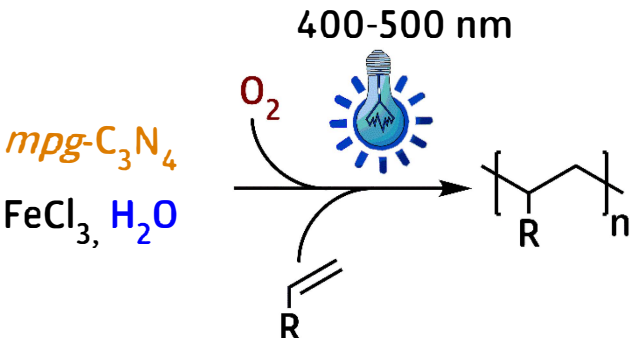


Figure S3: The photo-DSC trace of TEGDMA polymerized with *mpg*-C_3N_4 (a) and *g*-C_3N_4 (b).

Highlights

- Oxygen-Tolerant visible light induced free radical polymerization was succeeded
- Fenton reagent was generated by using graphitic carbon nitride.
- Surface area of the carbon nitride effected the efficiency of the photoinitiation


400-500 nm
O2
mpg-C3N4
FeCl3, H2O
R
R
n

Author Contribution Statement

Kerem Kaya: Methodology, Software

Baris Kumru: Methodology

Baris Kiskan: Conceptualization, Writing - Original Draft, Software

Bernhard V. K. J. Schmidt: Writing - Original Draft, Funding acquisition

Yusuf Yagci: Writing - Original Draft, Supervision, Funding acquisition